Synergistic Antioxidant Activity of Capsicum Oleoresin, Lecithin and Curcuminoids in Sunflower Oil

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Abstract: Essential fatty acids (EFAs) have the tendency to undergo autoxidation. Hence, the addition of antioxidants becomes a key step during their storage. Synthetic antioxidants are found to be toxic in nature. Recently, many investigations were carried out where EFAs were stabilized by natural antioxidants those can even replace synthetic antioxidant totally. In the present study, capsicum oleoresin, soy lecithin and curcuminoids were used to stabilize EFAs in refined sunflower oil. The study showed that the synergism of these natural antioxidants in proper proportion increased the shelf life of sunflower oil. Consequently, the nutritive value of EFAs was restored because of their effective stabilization and the natural antioxidants added for their stabilization provided the medicinal benefits.

Keywords: Antioxidants, Sunflower oil, Capsicum, Lecithin, Curcuminoids.

INTRODUCTION

Essential fatty acids (EFAs) are required dietary nutrients as they perform vital functions for good health and cannot be synthesized completely in human body [1]. The main sources of these EFAs are oils such as flaxseed, soybean, sunflower, safflower and fish oils [2]. Being highly susceptible to autoxidation, the storage of these oils becomes difficult. The process of autoxidation needs to be prevented to restore the nutritive value of EFAs. Generally, synthetic antioxidants such as tertiary butylhydroquinone (TBHQ), butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) are added to prevent the autoxidation but their safety has been questioned [3]. Accordingly, a safer antioxidant needs to be investigated.

Recent research has been concentrated on natural sources of antioxidants such as spices, herbs [4]. The presence of active components in spices has been demonstrated over the last 30 years [5]. Spices and condiments, though employed in small quantities, exert a considerable effect on the stability of fats and oils [6, 7]. Hence, it is worth to state that the use of these natural antioxidants is a promising substitute to the synthetic antioxidants.

The common household spices extensively used in India, capsicum [8] and curcuminoids [9] are known to have antioxidant effect. The capsicum was found to be effective antioxidant in oil [9] and margarine as well [10]. Herbalists have valued capsicum for its various therapeutic actions including anti-inflammatory, antiseptic effects [11], treatment of cutaneous allergy and neurological disorders [12]. Emerging studies have shown that capsicum is an effective medicine against neuropathic pain [13]. Capsaicinoids may have the potential for the weight loss [14] and also as an anticancer agent [15]. Similarly, curcumin, a major component of curcuminoids has medicinal properties against various diseases such as anorexia, coughs, diabetes, hepatic disorders, rheumatism and Alzheimer disease [16]. Curcuminoids are phytopharmaceuticals that have been shown to alleviate depressive symptoms [17] and an effective agent against wound healing [18].

It has been reported previously that curcuminoids alone revealed pro-oxidant effect [19]. However, the addition of these antioxidants in a suitable concentration can exert an antioxidant effect as a whole. The present study focuses to evaluate the antioxidant activity of capsicum oleoresin alone and in synergism with curcuminoids in sunflower oil. The work was further extended to study the synergistic activity of capsicum oleoresin, curcuminoids and soy lecithin, a well known antioxidant [20, 21] in the same oil.

MATERIALS AND METHODS

Materials

Refined sunflower oil without added antioxidant (RSFO) was received as a gift sample from M/s Cargill India Pvt. Ltd., New Delhi. The oil did not contain any added synthetic antioxidant. Soy lecithin was procured

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from M/s V.R. Chemicals, Mumbai. Capsicum oleoresin and curcuminoids powder were obtained from Kancor India Ltd., Angamaly South, India. All other chemical reagents and solvents were obtained from s.d. fiNE-CHEM LiMiTEd, Mumbai.

Analysis of Capsicum Oleoresin

The presence of capsaicinoids was checked by UV spectrometry (Shimadzu UV-1601) of capsicum oleoresin in isopropanol [22].

Preparation of Samples to Study Antioxidant Activity

The various blends of oil containing capsicum oleoresin (1.5%, 2%, 2.5%, 3% w/v) and its combination with soy lecithin (1.5% w/v) and curcuminoids (50 ppm) were prepared. The oxidative stability of oil blends was checked at 60°C for 30 days at regular interval of 5 days according to the AOCS Official Methods [23] by peroxide value (PV, Method Cd 8-53), *p*-anisidine value (*p*-A.V., Method Cd 18-90) and total oxidation (Totox) value (Method Cg 3-91). All the experiments were carried out in triplicate and the values were expressed as arithmetic mean of the experiments along with standard deviation.

The activities of natural antioxidants were compared with control sample and TBHQ (200 ppm) under the same conditions. The relative antioxidant activities were compared using Oxidative Factor (OXF) for antioxidants based on mean peroxide value of triplicate experiments using following formula [24],

$$OXF = \frac{\left(PV_{final} - PV_{initial}\right)_{antioxidant}}{\left(PV_{final} - PV_{initial}\right)_{control}}$$

where PVs indicate the mean values of all triplicate determinations of the peroxide value.

RESULTS AND DISCUSSION

Linoleic and linolenic acids are respectively 10 and 25 times more unstable as compared to monounsaturated oleic acid [25]. The deterioration of sunflower oil rich in linoleic acid can be prevented by using a suitable antioxidant. The antioxidants are phenolic compounds substituted by electron donating groups at *ortho* and/or *para* positions. They act by inactivating free radicals generated during autoxidation process by proton donation mechanisms [26]. In this context, easily available as well as non-toxic natural antioxidants like capsicum oleoresin, soy lecithin and curcuminoids were used as substitutes for synthetic antioxidant.

The presence of capsaicinoids in capsicum oleoresin was confirmed by the peak at 281 nm in the UV spectrum [22] of the capsicum oleoresin solution in isopropanol.

Oxidative Stability of Sunflower Oil in Presence of Capsicum Oleoresin

The peroxides are primary oxidation products that can further undergo degradation to form low molecular weight aldehydes and ketones. The radicals are prone to peroxidation and follow the chain reactions, typical of radicals [25]. Capsicum oleoresin contains a group of capsaicinoids like capsaicin, dihydrocapsaicin, nordihydrocapsaicin, homocapsaicin, homodihydrocapsaicin that act as conventional antioxidants by deactivating radicals. Semwal *et al*. [27] showed that capsaicin and dihydrocapsaicin reveal considerable antioxygenic activity when incorporated at the concentration of 100 ppm in sunflower oil. The solubility of capsicum oleoresin in RSFO was found to be 3%. The capsicum oleoresin under study contained 3.14% capsaicinoids. Consequently, capsicum oleoresin did not show significant antioxidant activity at lower concentration (200-800 ppm) since it did not provide sufficient amount of capsaicinoids. It showed significant antioxidant activity (Tables **1**, **2** and Figure **1**) at higher concentrations (2-3%) corresponding to 600-1000 ppm capsaicinoids. There was insignificant increase in antioxidant activity with increase in the concentration beyond 2.5% concentration.

Effect of Capsicum Oleoresin (2.5%), Lecithin and Curcuminoids on Oxidative Stability of RSFO

Curcuminoids exhibit keto-enol tautomerism in solutions, with up to 95% curcuminoids in the enol form depending on the solvent [28]. In alkaline conditions, curcuminoids rapidly decompose to ferulic acid and feruloylmethane [29] that further undergo hydrolysis to form vanillin and acetone. Masuda *et al*. [30] also supported autoxidation of curcuminoids. In neutral and acidic solutions (from pH 3 to 7), the keto form predominates that acts as H-atom donor. Thus, it is crucial to maintain these curcuminoids in the keto form by employing acidic conditions to utilize their antioxidant activity.

Initially, capsicum oleoresin (2.5%) was incapable to stabilize curcuminoids thereby showing peroxide formation same as that of RSFO (Tables **1**, **2** and Figure **2**). But as the study was continued, it showed marginal antioxidant activity in synergism with curcuminoids. However, it was lower than that of capsicum oleoresin alone. Though capsicum is a good source of phenolic acids [31], the amount was insufficient to stabilize curcuminoids. On the other hand, the same blend showed lower totox value. It indicated that the blend has potential to stabilize peroxy radical thereby reducing the formation of secondary degradation products like carbonyl compounds.

Capsicum oleoresin showed better antioxidant activity in synergism with lecithin. Furthermore, when the mixture of curcuminoids is added to the same blend, the antioxidant activity was improved. It was comparable to the activity of TBHQ (Figure **2**). Lecithin is known to prevent the autoxidation of oil by its action as an oxygen barrier between oil/air interface and also as a metal ion chelator [32]. The radical deactivating potential of capsaicinoids was accompanied by oxygen barrier from lecithin resulting in reduced peroxide formation.

The presence of free fatty acids from lecithin (acid value, 6.23 $mg.g^{-1}$) inhibited the degradation of

Table 1: Effect of Synergism of Capsicum Oleoresin with Lecithin and Curcuminoids on Oxidative Stability (Peroxide Formation) of Refined Sunflower Oil without Antioxidant (RSFO) at 60°C

Sample / Time (days)	OXF					
	5	10	15	20	25	30
RSFO + TBHQ	0.66	0.40	0.28	0.28	0.21	0.32
RSFO + 2% capsicum oleoresin	0.44	0.87	0.61	0.72	0.60	0.71
RSFO + 2.5% capsicum oleoresin	0.51	0.50	0.52	0.58	0.56	0.66
RSFO + 3% capsicum oleoresin	0.56	0.48	0.51	0.58	0.52	0.59
RSFO + 2.5% capsicum oleoresin + 50 ppm curcuminoids	1.16	1.04	0.85	0.75	0.79	0.72
RSFO + 2.5% capsicum oleoresin + 1.5% lecithin	0.83	0.63	0.63	0.51	0.47	0.47
RSFO + 1.5% capsicum oleoresin + 1.5% lecithin + 50 ppm curcuminoids	1.21	0.85	0.82	0.78	0.80	0.75
RSFO + 2% capsicum oleoresin + 1.5% lecithin + 50 ppm curcuminoids	1.02	0.76	0.74	0.64	0.52	0.62
RSFO + 2.5% capsicum oleoresin + 1.5% lecithin + 50 ppm curcuminoids	1.17	0.70	0.48	0.44	0.39	0.30

Table 2: Effect of Synergism of Capsicum Oleoresin with Lecithin and Curcuminoids on Oxidative Stability (Totox Value in meq/kg) of Refined Sunflower Oil without Antioxidant (RSFO) at 60°C

Sample / Time (days)	TOTOX†					
	5	10	15	20	25	30
RSFO	17.0±1.4	22.6±1.5	30.0±1.5	40.1±1.6	51.5±2.2	70.9±3.9
RSFO + TBHQ	6.3±0.9	8.2±0.8	11.2±1.0	14.0±1.1	14.5±1.6	26.3±2.8
RSFO + 2% capsicum oleoresin	11.1±1.0	15.0±1.0	19.8±0.9	29.1±1.6	33.3±1.7	51.0±2.5
RSFO + 2.5% capsicum oleoresin	9.2±1.2	12.7±1.2	17.5±1.3	24.8±1.5	30.5±1.7	47.1±2.4
RSFO + 3% capsicum oleoresin	9.3±1.1	12.5±1.3	16.9±0.7	23.8±1.2	28.9±1.4	43.2±2.2
RSFO + 2.5% capsicum oleoresin + 50 ppm curcuminoids	9.6±1.5	12.7±1.2	18.0±1.0	20.2±1.2	29.4±1.5	40.4±2.2
RSFO + 2.5% capsicum oleoresin + 1.5% lecithin	10.5±0.8	13.6±1.0	19.0±1.2	21.0±2.0	29.4±2.2	40.9±3.4
RSFO + 1.5% capsicum oleoresin + 1.5% lecithin + 50 ppm curcuminoids	12.8±0.7	15.2±1.2	17.6±0.9	21.7±1.1	29.6±1.6	40.9±1.8
RSFO + 2% capsicum oleoresin + 1.5% lecithin + 50 ppm curcuminoids	8.7±1.0	11.8±0.7	16.6±0.6	20.6±1.1	26.7±1.5	33.2±1.9
RSFO + 2.5% capsicum oleoresin + 1.5% lecithin + 50 ppm curcuminoids	8.1±0.6	10.4±0.9	14.7±0.5	16.6±1.3	17.8±1.6	29.1±2.2

† The values given are means of three consecutive experiments ± standard deviations

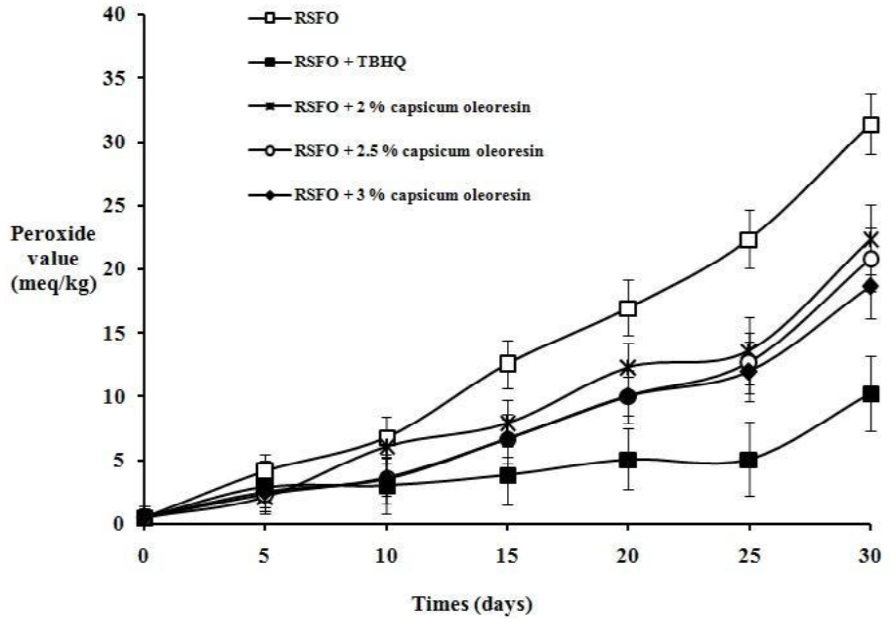

Figure 1: Effect of capsicum oleoresin on oxidative stability (peroxide formation) of RSFO at 60°C.

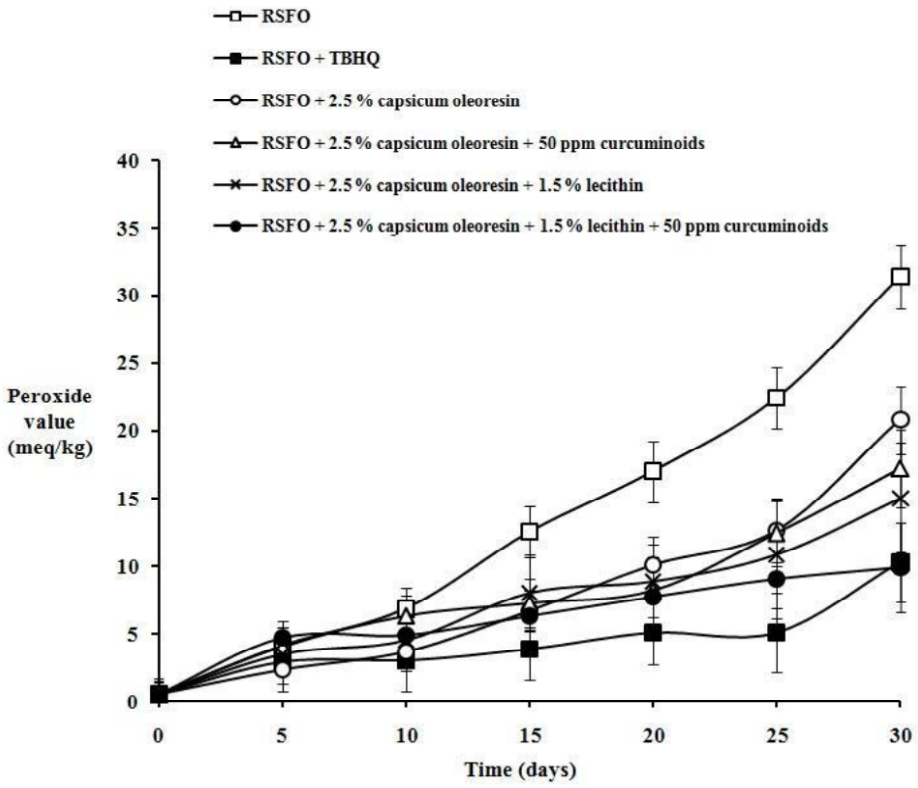

Figure 2: Effect of capsicum oleoresin, lecithin and curcuminoids on oxidative stability (peroxide formation) of RSFO at 60°C.

curcuminoids thereby maintaining them in keto form. A similar mechanism was shown by kalonji seeds extract as well that also inhibited the degradation of curcuminoids due to presence of free fatty acids [33]. As a result, lecithin, capsicum oleoresin and curcuminoids all acted by different mode of action and concurrently showed synergistic antioxidant activity. In addition, there was increase in antioxidant activity with increase in the concentration of capsicum oleoresin in presence of lecithin and curcuminoids (Tables **1** and **2**).

CONCLUSION

The synergistic antioxidant activity of capsicum oleoresin, lecithin and curcuminoids in appropriate quantity in refined sunflower oil was comparable to synthetic antioxidant. This effect was due to the combined action of the added antioxidants resulting in increased antioxidant potential than that expected from a mere additive effect. Natural antioxidants being the choice of consumers, can find better acceptability over synthetic antioxidants. With stabilization of essential fatty acids (EFAs) using such antioxidants in conjunction with their medicinal benefits, the consumers can enjoy the benefits of EFAs and therapeutic uses of natural antioxidants. Since these natural extracts containing antioxidants are normally used in household cooking, their taste will be familiar and hence acceptable.

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